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Review

Effect of climate change on humic substances and associated impacts on the quality of surface water and groundwater: A review

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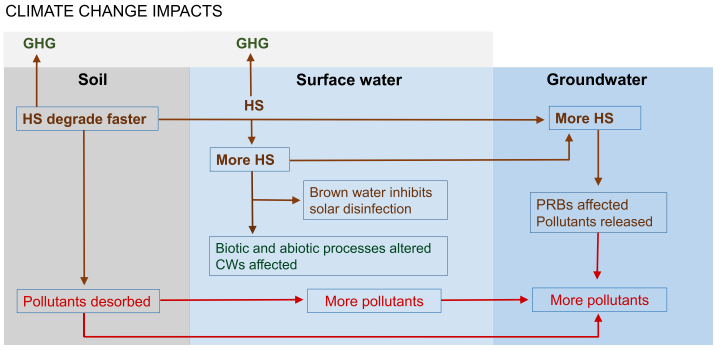
HIGHLIGHTS

- Humic substances (HS) play an important role in generation of greenhouse gases (GHG).
- Climate change (CC) enhances biodegradation of humic substances (HS).
- Microbial activity is stimulated and degradation of contaminants more efficient.
- Solar disinfection in surface waters is inhibited by increased presence of DOM.
- Pollutants may be desorbed and re-mobilized.

GRAPHICAL ABSTRACT



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ABSTRACT

Humic substances (HS), a highly transformed part of non-living natural organic matter (NOM), comprise up to 70% of the soil organic matter (SOM), 50–80% of dissolved organic matter (DOM) in surface water, and 25% of DOM in groundwater. They considerably contribute to climate change (CC) by generating greenhouse gases (GHG). On the other hand, CC affects HS, their structure and reactivity. HS important role in global warming has been recognized and extensively studied. However, much less attention has been paid so far to effects on the freshwater quality, which may result from the climate induced impact on HS, and HS interactions with contaminants in soil, surface water and groundwater. It is expected that an increased temperature and enhanced biodegradation of SOM will lead to an increase in the production of DOM, while the flooding and runoff will export it from soil to rivers, lakes, and groundwater. Microbial growth will be stimulated and biodegradation of pollutants in water can be enhanced. However, there may be also negative effects, including an inhibition of solar disinfection in brown lakes. The CC induced desorption from soil and sediments, as well as re-mobilization of metals and organic pollutants are anticipated. In-situ treatment of surface water and groundwater may be affected. Quality of the source freshwater is expected to deteriorate and drinking water production may become more expensive. Many of the possible effects of CC described in this article have yet to be explored and understood. Enormous potential for interesting, multidisciplinary studies in the important research areas has been presented.

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Contents

1. Introduction

"Climate" term refers to global, long-term (years or decades) environmental conditions, e.g. global average of temperature, humidity and rainfall patterns over seasons. "Climate change" term describes any change in climate conditions resulting from natural causes or human actions. It describes a broad range of global phenomena, which include the increased temperature trends (global warming) and other changes like rise in sea level; loss of ice mass and extreme weather events (NASA, 2018).

Changes in the Earth's climate have been happening since the Earth's generation. There have been seven cycles of glacial events until, about 7000 years ago, the last ice age ended and the modern climate era and human civilization began. Most of the past climate changes are believed to have resulted from very small variations in the Earth's orbit, which changed the amount of solar energy received by Earth (Lean, 2010). Since the early 20th century, especially since the late 1970s, an increasing temperature trend across the whole Earth, named as the global warming, has been observed (NASA, 2018). It has been concluded that, contrary to the past climate changes, Sun is not responsible for the increase in the Earth's temperature observed over the past 50 years. Instead, recent changes in the Earth climate are related to human activity and human-produced greenhouse gases, GHG (IPCC, 2014; Lockwood, 2009; NASA, 2018; Oreskes, 2004).

Most of GHG (CO_2, CH_4, N_2O and H_2O) occur naturally. The heat-trapping capacity of the naturally generated GHG has been known for a long time. There is ancient evidence showing that the Earth's climate responds to changes in GHG levels. For thousands of years, natural sources of GHG have been balanced by natural sinks. Human activity significantly contributes to emissions of all known GHG except for the H_2O vapor (Bousquet et al., 2006; IPCC, 2014; US EPA, 2016). It is believed now that human activity has upset the balance, which existed before the Industrial Revolution (IPCC, 2001, NASA, 2018; NASEM, 2017a; US EPA, 2017a, b).

Results of the latest studies seem to contradict the conclusion that human activity is the only cause of the observed climate change. It has been shown that a large proportion of climate variations could be explained by action of total solar irradiance (TSI) and cosmic rays (CRs) on the state of the lower atmosphere and other meteorological parameters (Alexandri et al., 2017; Biktash, 2017; Chapanov et al., 2017; Friis-Christensen and Lassen, 1991; Engels and van Geel, 2012; Kilifarska and Haight, 2005; Ma, 2017; Moreno et al., 2017; Wang et al., 2017). These reports indicate that the effects of solar, geophysical, and human activity on CC interact, and that more investigations are required in order to explain this complicated relationship. Whatever the reason, natural or anthropogenic, there is a large body of evidence that the Earth's climate is changing (IPCC, 2001; King, 2004) and that global warming is the main characteristic of this change (NASA, 2016).

Humic substances (HS) considerably contribute to global warming by generating GHG. Their role in the global warming has been extensively studied and reported (Section 2.2 below). On the other hand, CC affects HS, their structure and reactivity. Many topics, including the effect on the soil organic matter (SOM), its structure, microbial community as well as carbon storage and respiration response are still not fully understood (Bond-Lamberty et al., 2016). Much less attention has been paid so far to freshwater (surface and groundwater) pollution, resulting from the climate induced impact on HS and their interactions with soil and water pollutants.

This article starts with presentation of HS, their structure, reactivity and contribution to the generation of GHG. Subsequently, potential impacts of CC on the HS biodegradation, microbial activity in soil and water as well as freshwater pollution are reviewed. The effects include an inhibition of solar disinfection in brown lakes caused by an increased concentration of NOM, resulting from the enhanced degradation of HS and subsequent wash-up from the soil and sediment surfaces. The CC induced desorption from soil and sediments, as well as re-mobilization of metals and organic pollutants have been considered. Possible CC effects on the processes relevant to the in-situ surface water and groundwater remediation, including constructed wetlands (CWs), in-situ flushing and permeable reactive barriers (PRBs), have been discussed. This review concentrates on the impact of CC on processes occurring in natural environment and on the quality of freshwater resources. However, any deterioration in the source freshwater quality will affect the drinking water production. Therefore, CC effects on the drinking water treatment have been briefly described.

2. Humic substances (HS) and their role in CC

2.1. HS: structure and reactivity

HS are the major carbon pool in the biosphere, about 1600×10^{15} g C. They comprise up to 70% of soil organic matter, SOM (Grinhut et al.,

2007) and they represent about 50–80% of dissolved organic matter (DOM) in freshwater (Thurman, 1985), 25% of DOM in groundwater and a small fraction (0.7–2.4%) of DOM in ocean (Paul et al., 2004). HS play a very important role in ecosystems because they regulate the global carbon and nitrogen cycles. They are brown to dark colored mixtures, usually separated into three fractions based on their aqueous solubility: fulvic acids, humic acids, and humin. According to the current view (Piccolo and Conte, 2000; Piccolo, 2001), HS should be considered as supramolecular associations of heterogeneous and rather small molecules. HS dynamic conformation is weakly stabilized by hydrogen bonds and van der Waals interactions; it can be disrupted by weak organic acids (Peuravuori, 2005; Peuravuori et al., 2007; Piccolo and Conte, 2000; Piccolo, 2001, 2002).

HS structure depends on their origin and age and so it is difficult to characterize it on the molecular level (Hedges et al., 2000). However, many HS properties are well determined and some characteristics, regardless of their origin, are similar. HS contain various functional groups (Stevenson, 1994) and form complexes with metals and organic compounds (Aiken et al., 2011; Davies et al., 1997; Nriagu and Coker, 1980; Perminova and Hatfield, 2005; Sposito and Weber, 1986; Struyk and Sposito, 2001). They contain high amounts of stable free radicals (Paul et al., 2006a) which can react with various biotic and abiotic substances. They behave like colloids (Piccolo et al., 1996; von Wandruszka, 2000) and are known for the sorption abilities (Aeschbacher et al., 2012; Georgi et al., 2007, 2008; Niederer et al., 2007). HS regulate the growth of plants and microorganisms, act as biostimulants in horticulture and are the major component of organic fertilizers. HS catalyze biochemical reactions and have direct nutritive value, because their low molecular parts can be taken by aquatic organisms (Canellas et al., 2015; Piccolo, 1996). They are involved in environment processes, including redox reactions, sorption, complexation, fate and transport of heavy metals and organic pollutants, as well as the stabilization of soil structure. Toxicity of heavy metals to bacteria is often correlated to the free cations concentration. Formation of HS–metal complexes and adsorption of metal cations on the surface of HS (and iron oxyhydroxides) reduces toxicity of heavy metals by lowering the concentration of their free cations in water (Davies et al., 1997; Nriagu and Coker, 1980; Sposito and Weber, 1986; Struyk and Sposito, 2001, Lipczynska-Kochany and Kochany, 2009).

The association or binding of non-polar, hydrophobic organic molecules to HS increases the solubility and thus mobility of various contaminants. On the other hand, interactions between HS and organic pollutants may result in a complete immobilization and incorporation of some substances into HS (Bronner and Goss, 2011; Georgi et al., 2007, 2008; Pan et al., 2008; Polubesova and Chefetz, 2014). Microbes may be also adsorbed on HS. Thus, HS may affect the bioavailability of organic contaminants to bacteria by binding the microbes as well as the pollutants (Perminova and Hatfield, 2005; Van Trump et al., 2006). HS also play a significant role in the anaerobic biological processes by acting as electron donors, acceptors and electron shuttles. Bacteria can use HS as an electron donor or acceptor in anaerobic respiration (Coates et al., 2002; Heitmann et al., 2007; Lau et al., 2015; Lipczynska-Kochany, 2018; Martinez et al., 2013; Van Trump et al., 2006). Electron transfer to and from HS is fully reversible and sustainable over successive redox cycles (Klüpfel et al., 2014; Walpen et al., 2018).

2.2. HS role in CC: generation of greenhouse gases (GHG)

Most GHG (CO_2, CH_4, N_2O, and H_2O) have been generated through natural processes. For instance, CO_2 emissions originate from an ocean-atmosphere exchange, plant and animal respiration as well as soil respiration and decomposition. CO_2 is also created by volcanic eruptions and through underground volcanic magma. It is released through vents, porous rocks and soils, and water, which feeds volcanic lakes and hot springs (LeGrande et al., 2016; NASEM 2017b; Robock, 2000). The natural sources of CH_4 include wetlands and oceans (US EPA, 2017a) as well as eruptions of volcanoes (Etiope et al., 2007; NASEM, 2017b). Soils under natural vegetation are an important source of N_2O, which is also produced in oceans. H_2O vapor is the most abundant GHG. Large amounts of H_2O are released by volcanoes (LeGrande et al., 2016; NASEM 2017b; Robock, 2000) and by evaporation from oceans, lakes and rivers. H_2O acts as a feedback to the climate. It responds quickly to changes in conditions by precipitation as rain or snow, or evaporation back to the atmosphere (US EPA, 2017a, b).

There is evidence that HS in soil and wetlands significantly contribute to CC by producing GHG, including CO_2 (Fig. 1). Approximately 81% of the organic carbon resources is involved in the significant degradation of SOM and it results in increased CO_2 emissions from soils (Dalias et al., 2001; Davidson and Janssens, 2006; Jenkinson et al., 1991; Katterer et al., 1998; Kirschbaum, 1995, 2000, 2006; Lloyd and Taylor, 1994; Trumbore et al., 1996). According to Kirschbaum (1995), a 1 °C increase of temperature would lead to 10% carbon loss in areas with mean temperature about 5 °C, whereas the same temperature increase would lead to loss of 3% in areas where mean temperature is 30 °C. Therefore, important regional differences in the SOM loss and CO_2 production can be expected. In natural environments, carbon enters the soil in litter fall, root turn-over or death of individual plants, providing the substrate for the formation of SOM. The amount of HS in SOM is controlled by the HS production (input of plant and animal debris) and the rate of the degradation. Both, the SOM formation and degradation, are temperature-dependent. The change of the soil carbon storage in response to climate warming depends on how they are balanced relative to each other (Davidson and Janssens, 2006; Kirschbaum, 2000, 2006; Stergiadi et al., 2016; Von Lützow and Kögel-Knabner, 2009). Degradation of DOM within lakes and rivers may also impact climate if DOM is completely mineralized and emits CO_2 to atmosphere (Tranvik et al., 2009; Raymond et al., 2013).

Methane (CH_4) is the GHG with the global warming potential (GWP) 28–36 times higher than CO_2 on a 100 year time scale (US EPA, 2017b). 15–40% of the global CH_4 comes from wetlands, where microbial activity is fundamentally different from that in upland ecosystems (Yvon-Durocher et al., 2014). Wetlands cover approximately 6% of the Earth's land surface. They are transitional areas between land and water with the not always well-defined boundaries (US EPA, 2015). They represent about 12% of the global carbon pool and they play an important role in the global carbon cycle (IPCC, 1996). In addition to emission of GHG, wetlands also affect the climate by regulating air temperature through evapotranspiration (Pokorný et al., 2016).

Wetlands can serve as both, a carbon sink and source; they act as a long-term storage of CO_2, but they are also a large source of CH_4. In most upland soils organic carbon can be completely mineralized to CO_2 by microorganisms, using oxygen (O_2) as a terminal electron acceptor (TEA). In contrast, anaerobic decomposition in wetland soil involves many microbial processes generating both CO_2 and CH_4 as the final products of mineralization (Bartlett and Harris, 1993; Cao et al. 1998; Frolking and Roulet 2007; Keller and Bridgham, 2007; Keller et al., 2009; Yu, 2012). Wetlands (and sediments) contain a high content of HS, which act as electron acceptors for anaerobic microbial respiration, including anaerobic CH_4 oxidation (Blodau and Deppe 2012; Bridgham et al., 2006, 2013; Cervantes et al., 2000, 2011; Coates et al., 2002; Keller and Bridgham 2007; Keller and Takagi 2013; Lovley et al., 1996; Lipczynska-Kochany, 2018 and refs; Martinez et al., 2013; Valenzuela et al., 2017). Recently, Walpen et al. (2018) have observed that that electron transfer to DOM is fully reversible over an electrochemical reduction and subsequent O_2-reoxidation cycle. This finding supports previous reports (Klüpfel et al., 2014) that HS can act as re-generable electron acceptors, allowing holding large amount of CH_4 in wetlands, and not to release it to the atmosphere.

DOM carbon cycling has an influence on climate because degradation to CO_2 and CH_4 is one of the main sinks of DOM in boreal lakes and wetlands. However, its net effect on global warming is difficult to

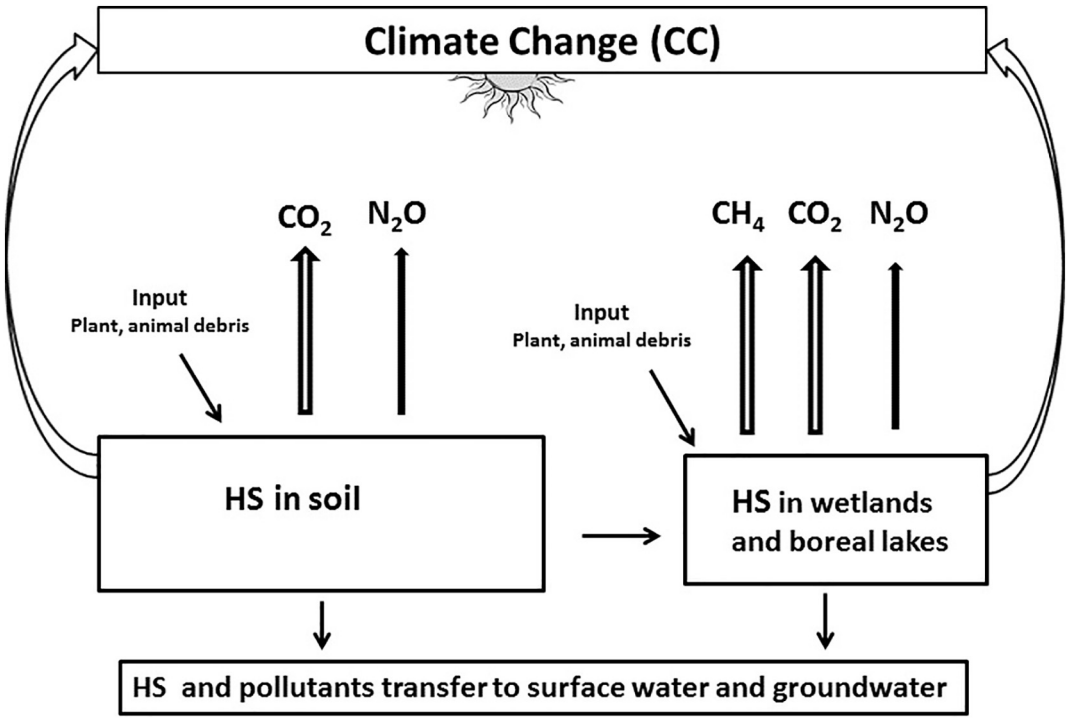

Fig. 1. HS impact on climate change (CC).

be predicted (Bertilsson and Tranvik, 2000). For instance, in places where water levels fall and organic matter is exposed to air, more CO_2 can be released from the formerly anoxic sediments which produced CH_4, more powerful greenhouse gas (Mortsch and Quinn 1996; Benoy et al., 2007). Depending on the balance between DOM losses to atmosphere versus transfer to the sediments, formation of CO_2 and CH_4 and their subsequent release to the atmosphere can increase or decrease, affecting the effect of climate change. Complex microbial processes, which play an important role in the global fluxes of CO_2 and CH_4, are likely to be affected by CC. However, is still unclear, whether alteration of these processes might result in a net positive or negative feedback for GHG emissions (Singh et al., 2010). It is also uncertain if wetlands HS will have a positive or negative feedback to the global climate system (Frolking et al., 2011; Junk et al., 2013; Lenhart 2009; Meng et al., 2012, 2016).

Nitrous oxide, N_2O, another potent GHG, has an atmospheric lifetime of about 100 years, and an almost 300-fold greater global warming potential (GWP) compared to CO_2 (US EPA, 2017b). The main sources of N_2O in soils are microbially-mediated processes, nitrification and denitrification. N_2O emissions can occur as direct emissions from natural and constructive wetlands (CWs) as well as from lakes and major river systems. DOM plays an important role in driving microbially-mediated denitrification (Philip and Townsend, 2010). Recent studies suggest that soil biochar amendment reduces soil nitrous oxide (N_2O) emissions and it leads to shifts in the soil microbial community composition (Harter et al., 2016; Jones et al., 2014).

3. Effect of CC on soil HS, their biodegradation and interactions with pollutants

3.1. Microbial degradation of HS

HS contribute to change in climate by generating GHG. On the other hand, CC has a significant impact on the HS structure as well as on their biotic and abiotic interactions (Fig. 2).

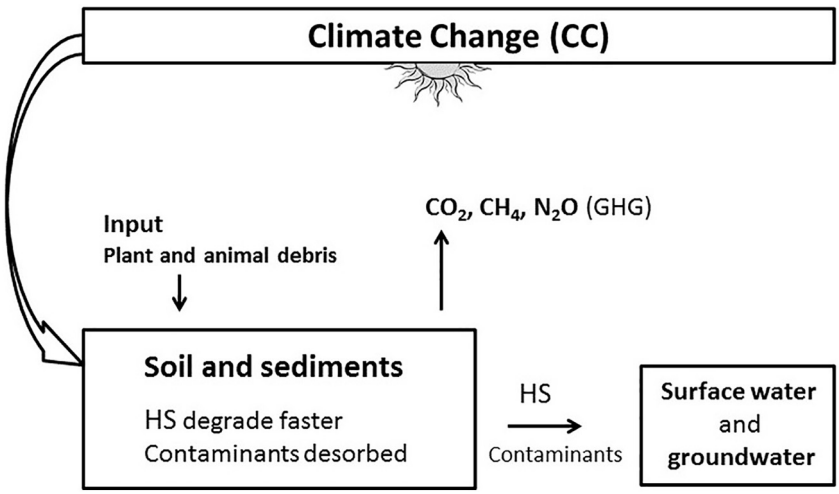

Fig. 2. Impact of CC on HS in soil and sediments.

In nature, the half-decay times ($t_{1/2}$) of HS can amount to thousands of years (Grinhut et al., 2007) and so it has often been assumed that HS are inert to biodegradation. However, even though HS belong to the most stable components of the soil organic fraction, their microbial decomposition constitutes a significant part of the turnover of organic carbon in soil (Lipczynska-Kochany, 2018; Martinez et al., 2013). Bacteria, actinomycetes and fungi (Grinhut et al., 2007) play an important role in many processes occurring in soil and can even mineralize HS. HS degradation in soil is dependent on environmental conditions, including temperature, soil moisture, pH, O2, presence of nutrients, redox potential, sorption capacity etc. (Castro et al., 2010; Kunc, 1988; Steinberg, 2003).

Increase in soil temperature could enhance HS degradation (Christ and David, 1996; Park et al., 2015; Rey et al., 2005) and increase the amount of substances available for microbial respiration (Balser et al., 2010; Dorrepaal et al., 2009; Zogg et al., 1997). Non-labile part of SOM is more sensitive to temperature than labile SOM, and so more DOM will be formed as a result of global warming (Cole et al., 2007; Kalbitz et al., 2000; Knorr et al., 2005; Ritson et al., 2014a, 2017).

In general, a rise in temperature corresponds to a rise in microbial activity (Balser et al., 2010; Mandal and Neenu, 2012; Whitaker et al., 2014). However, microbes live in complex communities composed of very different organisms, which are expected to respond to CC in a different way. CC may therefore alter species distributions and interactions among organisms (Classen et al., 2015; Rivkin et al., 1996; Whitaker et al., 2014; Zogg et al., 1997). In addition to temperature, the soil moisture and the frequency of wet/dry and freeze/thaw cycles, as well as changes in precipitation, can modify the soil aggregation. They may have potential important impacts on the availability of HS and, as a consequence, on the microbial structure and activity (Castro et al., 2010; Mandal and Neenu, 2012).

3.2. Interactions between HS and soil contaminants

Soils are receiving large quantities of trace metals from a wide variety of industrial wastes (Nriagu, 1996; Nriagu and Pacyna, 1988). When introduced into the environment, heavy metals tend to accumulate in soils and sediments because of their affinity for sorption processes (Su et al., 2014). Biogeochemical processes (sorption/desorption, complexation, dissolution/precipitation, and uptake/release by biota) control the mobility of heavy metals and thus the residence time in soils and water (Reeder et al., 2006). Although many of the most toxic substances introduced into the environment by human activity have been banned or restricted in use, many still persist, especially in soils and sediments. Sorption directly or indirectly controls all biotic and abiotic processes in soil, which affect metals and also organic pollutants (Barth et al., 2009; Bloomfield et al., 2006; Elzwayie et al., 2017; Ma et al., 2016; Smith et al., 2009; Sun et al., 2016; Wang et al., 2015; Wang et al., 2016; Whitehead et al., 2009). The interactions of HS with pollutants, especially sorptive processes, have been the subject of intense studies for several decades and are described in many original and review papers including Pan et al. (2008), Piccolo et al. (1992), Senesi and Miano (1995) and Werner et al. (2013).

Generally, sorption coefficients decrease with increasing temperature. This effect is inversely related to water solubility which, on the contrary, increases with temperature for most organic compounds (Delle Site, 2001; Jia et al., 2010; Tremblay et al., 2005; Wang et al., 2010). Through complexation and binding HS can enhance water solubility and mobility of metals and other pollutants (Sposito and Weber, 1986; Van Trump et al., 2006). Many studies demonstrated that pH, temperature and ionic strength have an important influence on the speciation of metal and binding with HS and other soil constituents (Benedetti et al., 1995; Ghabbour et al., 2001; Güngör and Bekbölet, 2010; Havelcova et al., 2009; Kjøller et al., 2004; Pehlivan and Arslan, 2006; Reeder et al., 2006; Sauve et al., 2000; Whitehead et al., 2009; Wijngaard et al., 2017). HS have found an application in remediation and bioremediation of soil contaminated with organic pollutants and metals (Davies et al., 1997; Dercova et al., 2007 Conte et al., 2005; Perminova and Hatfield, 2005; Sannino et al., 2013). One can expect that CC, which alters the structure and the reactivity of HS, would affect the efficiency of such treatments.

Complicated interactions between soil HS, oxides and clays (Vermeer et al., 1999) with microbes and environmental pollutants are strongly affected by environmental conditions including pH, temperature, ion strength and redox state (Van Trump et al., 2006). Climate induced changes in the structure of HS, resulting from their microbial transformations are also likely to alter the character of binding between HS and pollutants, what may lead to desorption and re-mobilization of metals and organic pollutants. Storm events, the discharged runoff and flooding might contribute to the problem and increase the concentration of toxic substances in aquatic systems.

4. Effect of CC on the quality of surface freshwater

4.1. Global consequences of CC

Consequences of CC are numerous and difficult to be predicted precisely. They include rising sea levels, increased emission, extreme weather events, and changes in bioavailability and environment stability (IPCC, 1996; NASA, 2018). It is expected that CC will seriously aggravate already existing freshwater problems. Freshwater, which is necessary for life, constitutes only about 2.5% of the water on Earth. Most of it is locked up in permafrost (ca 69%) and in the ground (30%). Surface water, in lakes and rivers, makes up about 1.2% of all freshwater (Shiklomanov, 1993). It is predicted that CC will intensify the water cycle. Warming is expected to bring an overall increase in rainfall and in extreme precipitation, including flash flooding. However, the anticipated rainfalls over dry areas will not necessarily make more water available because evaporation will increase (Donat et al., 2016). While some places may experience storm surges and longer droughts, other places may enjoy milder weather (Bond-Lamberty et al., 2016). Despite the predicted global increases in rainfall, CC is also expected to reduce rainfall in many already dry regions. According to the estimate of the IPCC, CC might lead to the situation, in which about one billion people in dry regions would suffer from the shortage of water (Bates et al., 2008).

CC is expected to change the amount of HS in surface waters and to alter their structure as well as change biotic and abiotic interactions with water contaminants. The impact of CC on HS and the surface freshwater quality is summarized in Fig. 3 and described in Sections 4.2–4.5 below.

4.2. Interactions between HS and microbes in freshwater

Dissolved HS play an important role in freshwater ecosystems (Steinberg et al., 2003, 2008). It can decrease pollutants toxicity through formation of various chemical complexes with xenobiotic compounds and metals. Dissolved HS are taken up and induce a variety of response reactions in organisms (Steinberg et al., 2006, 2009); they serve as a carbon and energy source for microorganisms in water and soil (Lipczynska-Kochany, 2018 and refs). DOM interacts with freshwater organisms in a variety of ways and it controls their growth (Steinberg et al. 2009). Many authors reported HS role in supporting bacterial production in lakes, rivers and blackwater marsh (Moran and Hodson, 1990; Moran et al., 2000; Steinberg and Bach, 1996; Tranvik and Höfle, 1987; Tranvik, 1988; Tranvik and Sieburth, 1989; Tranvik, 1990, 1992; Visser, 1985a, 1985b). For instance, Tranvik and Höfle (1987) reported that heterotrophic bacterial biomass produced on water from humic lake was double as compared to that on clear water.

Large rivers frequently receive inputs of DOM from soil and wetlands. CC is expected to alter conditions across the Earth and to influence the DOM export. CC induced variations in runoff and temperature will likely result in changes in the DOM structure and its

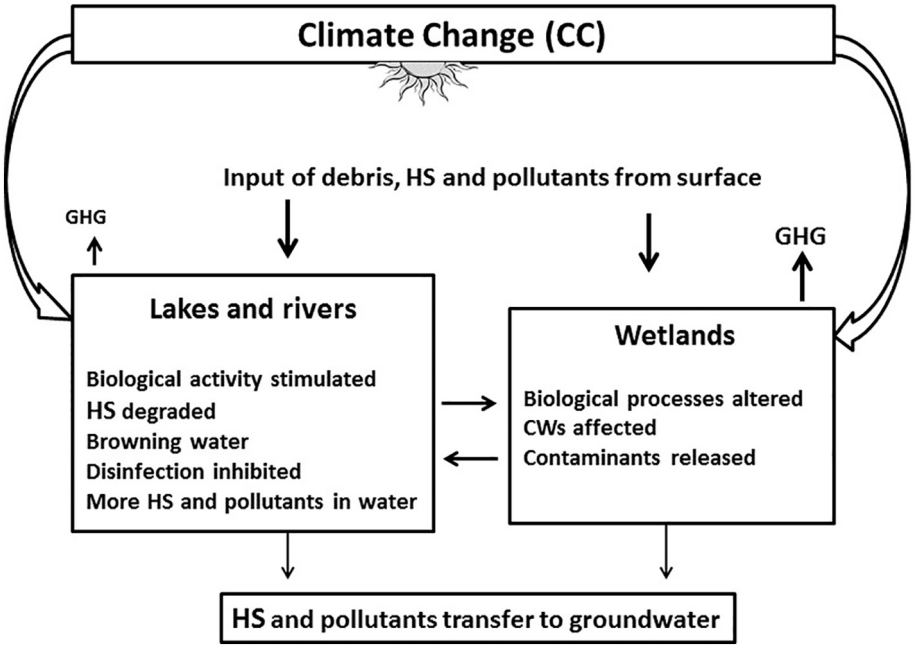

Fig. 3. Impact of CC on HS and surface freshwater.

concentrations in freshwater (e.g. Benoy et al., 2007; Christ and David 1996; Duan et al., 2017; Eimers et al., 2008; Porcal et al., 2009; Mortsch and Quinn, 1996; Porcal et al., 2015). During the last 30 years, an increase in DOM concentrations in lakes and rivers has been already observed in Europe and North America (Hongve et al., 2004; Evans et al., 2005; Freeman et al., 2001b, 2004; Porcal et al., 2009; Schindler et al., 1997; Vuorenmaa et al., 2006; Worrall and Burt 2004). Changes in DOM structure and concentration are expected to vary because, according to the CC models, the CC effects such as the frequency of storms, drought and runoff events, will depend on the region (Cox and Whitehead, 2009; Eimers et al., 2008; Evans et al., 2006; Tranvik and Jansson, 2001). Terrestrially derived DOM is decomposed by marine as well as estuarine bacterial communities (Esham et al., 2000; Rocker et al., 2012). Temperature is considered to be an important factor affecting microbial production and specific growth rate in estuarine, costal and freshwater ecosystems (Goldman et al., 2013; Shiah and Ducklow, 1994). It is therefore likely that CC will increase the amount of DOM in surface waters, enhancing the observed activity. As a result of CC (higher water temperature, changes in rainfall and increased nutrient inputs) harmful algal blooms in freshwater and in marine environments are expected to increase (Paul, 2008; Chapra et al., 2017). On the other hand, micro-algal grow may have a beneficial effect because micro-algae can be converted to biodiesel fuel, allowing reducing the use of carbon-based fossil fuels such as petroleum (Chisti, 2008; Pienkos and Darzins, 2009; Lardon et al., 2009; Mata et al., 2010; Sayre, 2010).

4.3. HS and pollutants in surface waters

Effects of HS on biodegradation in soil have been extensively investigated. However, much less attention has been so far paid to effects of HS and CC on the toxicity and biodegradation of organic pollutants in freshwater ecosystem and in sediments (Delpla et al., 2009; Noyes et al., 2009). Results of few studies confirm that HS-pollutants interactions can alter contaminants toxicity and their biodegradation (Tranvik and Höfle, 1987).

Climate warming and changing rainfall patterns are expected to affect fate and behavior of organic pollutants in surface water. Most of chemical reactions and microbial processes, including DOM degradation and its interactions with contaminants, are faster at higher temperature (Bloomfield et al., 2006; Sjerps et al., 2017; Whitehead et al., 2009, Section 3.1 herein). CC is also expected to influence transport and redistribution pathways of pollutants, because adsorption processes are temperature dependent and so directly affected by CC (Kallenborn et al., 2012; Ripszam et al., 2015). More intense extreme events like storms and rainfall as well as flooding may release pollutants adsorbed to sediments and soil, and transport them to rivers, lakes and oceans. Melting of polar ice caps and permafrost may remobilize pollutants stored in snow and ice and, as a result, bring them back to aquatic ecosystems (Spezzano, 2012). DOM binds nutrients (N, P, Fe), metals and other pollutants, affecting their toxicity and bioaccumulation (Section 2.1). Under altered environmental conditions, the DOM structure and its interactions with contaminants may change leading to the release of bound nutrients and pollutants, including toxic free metal cations (Bertilsson and Tranvik, 2000; Kelton et al., 2007; Shiller et al., 2006; Stumm and Morgan 1995; Vähätalo et al., 2003).

4.4. Effect of sunlight on the HS-microbial interactions in freshwater

In natural waters, HS represent the main fraction of DOM that absorbs solar radiation (Paul et al., 2004, 2006a). Sunlight affects the HS – microbial interaction in a number of ways and both, benefits and adverse effects on aquatic organisms have been reported (Amador et al., 1989; Bertilsson and Tranvik, 2000; Granéli et al., 1996; Osburn et al., 2001; Paul et al., 2004; Porcal et al., 2015; Scully et al., 2003a, 2003b; Steinberg, 2014).

Increase of temperature and an enhanced biodegradation of SOM lead to an increase in the production of DOM, while the flooding and runoff export DOM from soil to rivers and lakes. Any change in DOC concentrations and properties may affect biological, chemical and photochemical processes taking place there. The brown DOM in lake and rivers absorbs solar light and undergoes photochemical reactions which modify its chemical properties.

Photolysis of DOM produces bioavailable low molecular organic compounds, which serve as organic nutrients for heterotrophic bacteria and it can release the DOM-bound inorganic nutrients, stimulating the microbial grow (Bertilsson and Tranvik, 1998, 2000; Paul et al., 2004; Tranvik et al., 2009). Therefore, the increased concentration of DOM in water may have a beneficial effect because DOM stimulates activity of bacteria degrading organic pollutants. On the other hand, sunlight can

damage microorganisms (Scully et al., 2003a, b). In addition to direct photolysis, microbes can be destroyed by free radicals released during the photo-irradiation of DOM (Steinberg, 2014).

An increase in browning of the surface waters, caused by the HS washed from the surrounding land may have an adverse effect on the water quality. It has been recently observed that an increase of the amount of DOM resulted in increased absorption of solar ultraviolet rays, prevented light from penetrating water and killing pathogens. In some cases, browning decreased the ability of sunlight to disinfect water by a factor of 10. Thus, an increase in browning of the surface waters, caused by DOM washed into the lake from the surrounding land may have an undesirable effect for drinking water supplies (Williamson et al., 2017).

4.5. Surface water remediation and production of drinking water

4.5.1. Surface water pollution

It is expected that changes occurring as a result of CC will have a significant influence on the freshwater quality (Delpla et al., 2009). Surface water acts as a receptor of pollutants, which are washed out and carried by the surface runoff. They may include fuel and oil, detergents and fertilizers and various kinds of litter. Rise of temperature will enhance soil microbial activity and production of DOM (Kalbitz et al., 2000; Section 3.1), which will be washed out from soil and wetlands to freshwater (Evans et al., 2005; Freeman et al., 2001a; Mo et al., 2016; Ritson et al., 2014b; Ritson et al., 2017; Worrall et al., 2003). Intense downpours can wash soil HS (Shang et al., 2018) and desorbed pollutants (Section 3.2 herein, Chou et al., 2018) into water sources and it may complicate water treatment processes. On the other hand, drought conditions and lower stream flow can aggravate these problems by concentrating pollutants and limiting dilution.

In many places, surface water pollution is a serious problem and various remediation techniques have been applied (e.g. Li and Chu, 2003; Borin and Tocchetto, 2007; Cao et al., 2012; Centi and Perathoner, 2003). Water treatment may be conducted using physical, chemical, and biological treatment technologies (Hamby, 1996; Wang et al., 2012), using ex-situ or in-situ methods. In the ex-situ approach, contaminated water is removed to be treated elsewhere, while in-situ remediation it is treated at the polluted site. Water remediation processes are designed to meet standards based on historical climate conditions. Under CC conditions, the existing technologies may have to be modified (Pyke et al., 2011).

4.5.2. Natural and constructed wetlands (CWs)

Bioremediation technologies (i.e. remediation using aquatic plants, aquatic animals and microorganisms, including bacteria and fungi) have been considered to be particularly attractive as in-situ methods for the treatment of contaminated surface water. Constructed wetlands (CWs) are fully human-made wetlands for wastewater treatment. They use natural wetland processes, associated with wetland hydrology, soils, microbes and plants. Potential of wetland plants to treat wastewaters was recognized in Germany in the early 1950s (Seidel, 1955; Vymazal, 2011). Since the late 1960s, when the first full-scale systems were created, various constructed wetlands (CWs) and semi-natural treatment wetlands (SNTWs) (Kadlec and Wallace, 2009; US EPA, 2015; Vymazal, 2011) have been used to treat wastewater in many countries (e.g. Ateia et al., 2016; Brix, 1997; Chazarenc et al., 2015; Ghrabi et al., 2011; Mitsch and Gosselink, 2007; Wu et al., 2015a, 2015b; Tamiazzo et al., 2015). CWs, SNTWs as well as artificial floating islands (AFs) can be used to treat collected wastewater from various sources, including municipal and domestic wastewaters (Kim et al., 2016; Vymazal, 2011), industrial and agricultural wastewaters, stormwater runoff and landfill leachate (e.g. Kadlec and Wallace, 2009; Chang et al., 2017; Deng and Ni, 2013; Morató et al., 2014; Sun et al., 2017; US EPA, 1996; Vymazal, 2013, 2014; Zhao et al., 2012). These methods can be used as the only treatments but they may also be applied in a combination of physical, chemical and biological processes (Kim et al., 2015; Liu et al., 2015; US EPA, 1996; Vymazal, 2013, 2014; Wu et al., 2015b), including a combination of biological lagooning with a solar driven photo-Fenton reaction (Silva et al., 2015) as well as CWs with microbial fuel cells (MFCs (Doherty et al., 2015). Another novel system has been proposed by Jasper and Sedlak (2013) who have demonstrated that open-water cells in unit process treatment wetlands can use sunlight to remove trace organic contaminants from municipal wastewater.

Construction and applications of wetlands to surface water treatment have been extensively studied and described in numerous other original and review articles (e.g. Cao et al., 2016; Chen et al., 2016; Chyan et al., 2016; Corbella and Puigagut, 2018; Hernández-Crespo et al., 2017; Hijosa-Valsero et al., 2016; Jácome et al., 2016; KKivaisi, 2001; Li et al., 2014; Lin et al., 2015; Lizama et al., 2011; Martín-Monerris et al., 2013; Odinga et al., 2013; Papaevangelou et al., 2016; Ruan et al., 2006; Sundaravadivel and Vigneswaran, 2010; Tu et al., 2014; Uggettia et al., 2016; Vymazal, 2010, 2014; Vymazal and Březinová, 2015; Zhang et al., 2014, 2015).

Both, natural and constructed wetlands are shallow water bodies, vulnerable to climate change. They are sensitive to changes in their water supply (IPCC, 1996) and so they may be strongly affected by alterations in the hydrological regimes and precipitation. Other CC related factors may also play an important role. They include an increased temperature (Kadlec and Reddy, 2001), changed evapotranspiration, biogeochemistry, amounts of suspended sediment loadings (Burkett and Kusler 2000) and increases in the frequency of extreme climate events. CC induced environmental changes are likely to affect CWs bioremediation by affecting aquatic organisms (Steinberg 2003a; Lipczynska-Kochany, 2018 and refs; Section 3.1 herein), as well as their interactions with HS and pollutants (Section 3.2 here).

Many wetland processes, including microbially mediated HS decomposition and nitrogen cycling reactions (mineralization, nitrification, and denitrification), are affected by temperature (Hu et al., 2010; Kadlec and Reddy, 2001; Liu 2013). The coastal wetlands, such as mangroves, might be also influenced by the rising of sea levels (Barrosa and Albernaza, 2014; Christ and David, 1996; Duan et al., 2017; Eimers et al., 2008; IPCC, 1996; Porcal et al., 2009; Rey et al., 2005).

Various processes, biological, chemical or physical, occurring in the complex wetland systems, overlap and interact. They take place within the vegetation, the water column, and in the soil and involve plants, microorganisms, soil matrix and pollutants in wastewater. These complex processes are still not well understood (Stottmeister et al., 2003). However, it is likely that CC influence on vegetation, biological activity and water chemistry (pH, alkalinity, temperature and dissolved oxygen) may have a strong effect on the wetland performance (e.g. Lizama et al., 2011; Paing et al., 2015; Stefanakis and Tsihrintzis, 2012). As a result of CC, adsorbed on soil and sediments heavy metals and other contaminants, may be released back to water. Storm events may affect constructed (and natural) wetland discharges (Taylor et al., 1993, 2013). Most of the processes occurring in wetlands are expected to be affected by CC, but their responses to CC will likely vary, depending on the region. The effect of CC on wetlands may be complex and difficult to predict (e.g. Champagne, 2008; IPCC 2001, 2014; Erwin, 2009; Junk et al. 2013; Kadlec and Reddy 2001; Paul et al. 2006b).

4.5.3. Production of drinking water

HS stimulate microbial degradation of pollutants and they play a beneficial role in remediation of soil (Section 3.2 herein), wastewater and groundwater (e.g. Lipczynska-Kochany and Kochany, 2008a, 2008b, 2009, 2011; Section 5.2 herein). Application of HS in natural remediation of surface water, highly contaminated with nuclear waste has been also reported (Aleksandrova et al. 2010). However, HS presence in drinking water is unwanted. They contribute to odor, color, taste as well as to acidity problems in water supplies. They are precursors of harmful

(Singer, 1999) disinfection by-products (DBPs) (Bond et al., 2011, 2012; Chen and Westerhoff, 2010; Kim and Yu, 2007; Uyak et al., 2008).

During the past 20 years, topics related to the presence of HS in drinking water have been studied by many researchers (e.g. Hongve et al., 2004). Extensive research on the HS removal from water has been conducted using various treatment methods, including coagulation, filtration and advanced oxidation processes. Results have been described in numerous original and review papers (e.g. Domany et al. 2002; Lamsal et al., 2011; Levchuk et al., 2018; Lowe and Hossain, 2008; Matilainen and Sillanpää, 2010; Matilainen et al., 2010; Murray and Parsons, 2004; Philippe et al., 2010; Stanford and Majeda Khraisheh, 2009).

As a result of CC, the quality of the source freshwater is expected to deteriorate. Drinking water production facilities are not always designed and equipped to handle the increased concentrations of DOM and other contaminants. They may need to adapt their processes to deal with consequences of frequent occurrences of extreme weather and with variable DOM concentrations. Thus, modifications of the infrastructure might be required and higher cost of drinking water production can be expected (Delpla et al., 2009; Raeke et al., 2017; Ritson et al., 2014a, 2014b; Ritson et al., 2016).

5. Effect of CC on the quality of groundwater and its remediation in-situ

5.1. Effect of CC on groundwater recharge and quality

Globally, groundwater is the source of one third of all freshwater withdrawals, supplying an estimated 36%, 42%, and 27% of water used for domestic, agricultural, and industrial purposes, respectively (Shrestha and Pandey, 2016). It is the world's largest reservoir of freshwater and it plays an important role in sustaining ecosystems and enabling human adaptation to climate variability and change. CC is expected to have a significant influence on soil water and temperature, as well as on subsurface hydrological and thermal processes (Green et al., 2011; Menberg et al., 2014). However, research on the CC impact on water systems has been focused mainly on the surface water, while potential effects on groundwater have received much less attention (Aslam et al., 2018).

The CC has a potential to affect both the quality and quantity of groundwater, predominantly through impacts on recharge and evapotranspiration. Groundwater is recharged naturally by rain and snow melt and by interactions with surface water (rivers, lakes and wetlands). Soil moisture is also an important factor in the groundwater recharge process (Balek, 1988; Sophocleous, 2004). Groundwater and surface water used to be considered separate entities, and investigated individually. However, processes occurring in the transition zones may affect transport, degradation, transformation, precipitation, and/or sorption of contaminants. Results of studies on exchange processes between groundwater and surface water have shown that such interactions may have a significant impact on the water quality of either of these hydrological zones (Kalbus et al., 2006; Keery et al., 2007; Sophocleous, 2002; Stegen et al., 2016).

Any changes in the regime and quantity of precipitation, together with changes in temperature and evapotranspiration, have a significant influence on the groundwater recharge. Most studies on the CC effects on groundwater have focused on processes that affect input (recharge), output (discharge), changes in storage, as well as the associated physical processes which control subsurface-water flow. It is predicted that, as a result of CC, the overall rate of groundwater recharge may increase. The higher intensity and frequency of precipitation is predicted to contribute significantly to the surface runoff, while evapotranspiration rate may increase as a result of global warming. However, it is also expected that climate-related changes to the groundwater recharge, storage, and base flow discharge, will depend on local conditions. There may be dry and semi-dry areas where aquifer recharge rates are low and demand for groundwater supply is high, while in areas where permafrost or glaciers melt, the groundwater recharge will increase (Dragoni and Sukhija, 2008; Pitz, 2016). Results of studies on the potential CC effect on the groundwater recharge have been described in a number of original and review articles (e.g. Earman and Dettinger, 2011; Holman, 2006; Jyrkama and Sykes, 2007; Mileham et al., 2009; Meixner et al., 2016; Smerdon, 2017).

CC is expected not only affect recharge and (discharge), but also to influence the quality of groundwater (Dragoni and Sukhija, 2008, Green et al., 2011; Taylor et al., 1993, 2013; Taylor, 2014). The relation between CC and groundwater is considered more complicated than that with surface water. Groundwater aquifers have a high storage capacity and are believed to be less sensitive to CC than surface waters. However, groundwater temperature may be more sensitive to climate warming than previously believed. Recent reports indicate that increasing groundwater temperature may have a significant influence on groundwater and river ecology (Green et al., 2011; Menberg et al., 2014; Pitz, 2016). Relatively few studies on CC and its influence on groundwater have focused on processes, which may affect groundwater quality. They include investigations of CC effects on pesticide fate and transport in the subsurface (Bloomfield et al., 2006).

HS in groundwater originate from recharge or in-situ generation by partial degradation of sedimentary organic matter, including lignite. HS concentration and composition depends on the recharge conditions, affected by CC (Artinger et al., 2000; Buckau, 2005). Resulting from CC, expected intense downpours can wash out soil HS and desorbed pollutants not only into surface water but also to groundwater. Expected CC impacts on the groundwater quality have been summarized in Fig. 4.

HS play a key role in the transport of pollutants, including heavy metals and radionuclides. The CC induced changes in the structure and quantity of HS in groundwater may alter interactions between metals, HS, soils and sediments (Kjøller et al., 2004). The sorption of HS on oxides and clay minerals is known to change the physicochemical properties of relevant interfaces (Gu et al., 1995, 1996) and it is affected by pH changes Jiang et al., 2014). HS form complexes with iron oxides through various types of functional groups and they can sorb to mineral surfaces (e.g. Tipping, 1981; Liu et al. 2008). HS can donate electrons to a number of dissolved and solid Fe (III) compounds (Bauer and Kappler, 2009) and magnetite (Sundman et al., 2017), resulting in the reduction and subsequent dissolution of minerals. HS-induced dissolution of minerals may result in remobilization of contaminants previously adsorbed on its surface. CC may have a significant impact on these complex environmental equilibria. Pollutants can be also adsorbed on HS and form stable aqueous complexes, what may impact their removal (Klausen et al., 2003; Liu et al., 2008; O'Loughlin et al., 1999; Sun et al., 2016).

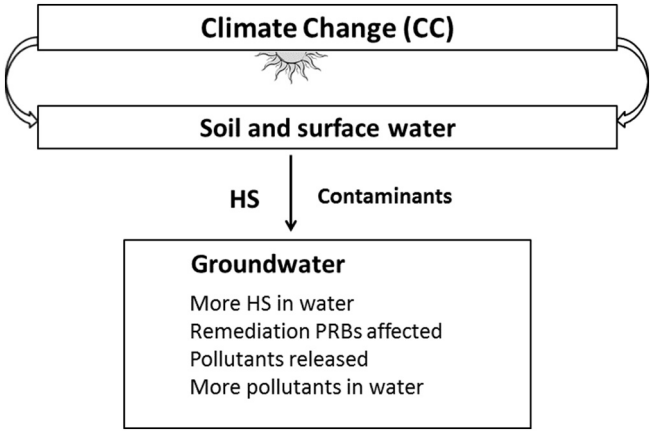

Fig. 4. Impact of CC on groundwater.

It is expected that changes in DOM composition may have an influence on the fate of organic pollutants, including polycyclic aromatic hydrocarbons (PAHs) (Chen et al., 2017; Haftka et al., 2010; Hur et al., 2014). Metals, and other pollutants, adsorbed on iron minerals can be re-mobilized and released to groundwater. It may be therefore expected that any changes in DOM concentration in groundwater systems will have a large effect on the groundwater pollution (Weng et al., 2009).

5.2. Groundwater remediation in-situ

It is very likely that extreme weather events, caused by CC, will lead to reduction of surface freshwater. In this situation, groundwater will be critical to relieve the serious freshwater problems. People in water-scarce areas will become increasingly depended on groundwater. Therefore, the availability and quality of groundwater are of a great importance.

Many groundwater sites are contaminated with complex mixtures of various pollutants, including chlorinated solvents, fuels, metals and/or radioactive materials. Since 1970s, polluted sites have been treated using the pump-and-treat systems, i.e. by pumping-out groundwater from the subsurface, followed by an above ground treatment and a discharge back into the ground. As a result of pumping, the groundwater level is lowered, leaving remaining pollutants adsorbed to the soil. When, after the treatment, groundwater returns to its previous level, adsorbed contaminants dissolve, what is called the "rebound" (Nyer, 2000a; US EPA, 1996). It is possible that major rain or flooding events, which will likely become more frequent under CC, may affect such rebounds.

More recently, various at the site (in-situ) remediation technologies have been developed. Such methods do not need any extraction of contaminated groundwater out of the ground. Instead, the remediation is carried out directly at the contaminated plume (Naftz et al., 2002; Nyer, 2000b). A significant interest in natural attenuation of metals and organic pollutants in soil and in aquifers has been observed (Bekins et al., 2001; Bourg et al., 1992; NRC, 2000; Wang and Mulligan, 2006; Wiedemeier et al., 1999). Natural attenuation is defined by the US Environmental Protection Agency (US EPA) as "a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater" (Rittmann, 2004). The natural attenuation processes are conducted in-situ and they include biodegradation; sorption and chemical or biological stabilization, transformation, or destruction of pollutants. These processes are expected to be influenced by CC.

HS and HS-based products hold a great promise as reactive agents for in-situ remediation. They can perform multiple functions in biotic (Lipczynska-Kochany, 2018) and abiotic processes. Their interactions with pollutants and living organisms can be used in remediation of soil and groundwater. An extensive overview of HS properties and their potential applications have been given by Perminova and Hatfield (2005). Properties of natural HS depend on their origin and so the reactivity of HS from different sources may vary significantly (Angst et al., 2018). Therefore, a concept of a chemical modification to design the HS materials of a desired remedial activity has been introduced. Manufactured HS, with enhanced the natural HS properties, have been described by Perminova et al. (2004, 2011, 2012, 2014) and Volikov et al. (2016a, b).

Permeable reactive barriers (PRBs) and in-situ flushing are considered to be the most promising technologies applying HS (Perminova and Hatfield, 2005). In-situ flushing involves the injection or infiltration of an aqueous solution into a zone of contaminated soil or aquifer to attenuate metals and organic pollutants in soils and aquifers (Nyer, 2000b). HS are used as flushing agents to treat sites contaminated with diesel fuel, PAHs and other organic contaminants (Conte et al., 2005; Georgi et al., 2007; Lesage et al., 2001; Van Stempvoort and Lesage 2002; Van Stempvoort et al., 2002a, b, 2005). HS act as natural surfactants allowing for desorption of the organic compounds from the soil and sediments, and make them more available for biodegradation. However, under changed conditions, dissolved HS can adsorb to soils and aquifer materials, resulting in re-immobilization of pollutants.

HS are also known to bind to mineral surfaces and to metals (e.g. Davis, 1982, 1984; Davis and Leckie, 1978; Ho and Miller, 1985; Kerndorff and Schnitzer, 1980; Tipping, 1981). The interactions between HS, metals and minerals are strongly dependent on a number of factors, including pH (e.g. Ho and Miller, 1985; Kerndorff and Schnitzer, 1980). The mobility of a metal with affinity for HS is determined by the mobility of HS. In groundwater, HS can decrease mobility of HS-bonded metals, if conditions favor sorption of HS to mineral surfaces. However, when conditions favor mobility of HS, mobility the HS-complexed metal may be enhanced. Depending on geological conditions, HS could be used to mobilize some metals or it could be used to enhance the sorption of other metals (Petrović et al. 1999).

It has been concluded that an in-situ approach for remediation of groundwater plumes could be based on the injection of HS into the aquifer, enhancing attenuation of some metals in the subsurface (Petrović et al., 1999; Wang and Mulligan, 2006; Denham et al., 2014, 2015). Under the groundwater conditions typical of many metal and radionuclide contaminant plumes, HS sorb well to mineral surfaces. Wan et al. (2011) have demonstrated that peat and soil HS, when sorbed to Savannah River Site soils, enhanced the sorption of uranium under acidic conditions (pH = 3.0 to 4.5). Denham et al. (2014, 2015) have also concluded that the injected HS is a potential attenuation-based method for in-situ remediation of acidic waste plumes containing uranium, iodine I-129 (but not for strontium, Sr-90). One should note though that the HS adsorption to sediment minerals varies with pH. Interactions between metals and HS are dependent on a number of factors, including pH. It is therefore possible that CC induced changes in the aquifer conditions, might lead to release of some HS and re-mobilize bonded metals. Careful monitoring would be therefore required and some corrections of the treatment may be needed.

Injection of dissolved HS, followed by a subsequent injection of acid, has been proposed as a method for creating a permeable reactive barrier, PRB (Oeste and Kempfert, 1996; Palmer, 2000; Thiruvenkatachari et al., 2008). PRBs filled with HS have been also reported by Balcke et al. (2005), Kopinke et al. (2005), Wang and Wang (2011). Humus degradation in soil is dependent on environmental conditions including temperature, soil moisture, pH, O_2, redox potential, sorption capacity, etc. (Schmidt et al., 2011, Section 3.1 herein). Thus, CC induced changes of these conditions are likely to affect the performance of HS PRBs.

CC may also affect the performance of PRBs filled with other materials, including iron oxides and metallic iron (Gheju, 2017; Henderson and Demond, 2007; Obiri-Nyarko et al., 2014; Scherer et al., 2008). Under environmental conditions, iron undergoes corrosion (Evans, 1981; Lipczynska-Kochany et al., 1994; Sato, 1989). At acidic and anoxic sites, attenuation proceeds mainly through reduction and immobilization on the iron surface (Matheson and Tratnyek, 1994; Tratnyek et al., 2003). However, at neutral pH, corrosion products become important. Presence of iron oxides on the zerovalent iron (ZVI) PRBs has been demonstrated in many lab and fields experiments (e.g. Farrell et al. 2001; Furukawa et al., 2002; Jiao, et al., 2009; Phillips et al., 2003; Wilkin et al., 2005; Su, 2007). Pollutants are removed from groundwater by adsorption/co-precipitation on the corroding iron surface (Noubactep, 2010), along with redox transformations mediated by iron (hydr)oxides coating on the surface of iron (Johnson et al., 1998; Scherer et al., 1998; Ritter et al., 2002). The ZVI PRB technology has been described in many original and review articles (e.g. Ghauch, 2015; Gheju, 2017; Guan et al., 2015; Henderson and Demond, 2007; ITRC, 2011, Noubactep, 2015; Sun et al., 2016). However, there has been little interest so far in the potential effect of CC on the performance of PRBs.

Warner (2007) noted that the climate-induced shifts in hydraulic gradients (resulting from shifting rainfall patterns, rising sea levels,

and fluctuating river levels) may be a reason for concern. He suggested that site design should take under consideration possible shifts in the hydraulic gradient caused by CC. Nevertheless, many other environmental factors may also have an effect on the PRBs performance. They include characteristics of local condition e.g. temperature, pH, dissolved oxygen, as well as water chemistry (e.g., anions, cations, HS) and presence of microorganisms. These influences, still not well understood, should not be considered individually isolated because, in natural systems, they usually affect each another (Sun et al., 2016).

The iron oxide water interface is a very dynamic region characterized by sorption, desorption, growth, and dissolution processes (Brown et al., 1999; Cornell and Schwertmann, 2003). Adsorption of contaminants on iron hydroxides, and interactions with HS, depend strongly on pH because the surface chemistry and the surface charge of the iron hydroxides oxides vary. Removal of pollutants adsorbed on oxides surface is strongly influenced by pH and temperature. Changes in these conditions may be critical for the release of metals (Jiao, et al., 2009; Kumar et al., 2015) and other pollutants immobilized on the PRBs surface or on the iron minerals in groundwater sediments.

Transformation of pollutants adsorbed on iron oxides can be enhanced by iron reducing microbes (Van Nooten et al., 2008; Philipps et al., 2010), whose growth is dependent on pH, oxygen and temperature (ITRC, 2011). Presence of sulfate-reducing bacteria in or around iron barriers and the subsequent formation of iron sulfides can also increase transformation of contaminants (Lipczynska-Kochany et al., 1994; Kumar et al., 2015; Van Nooten et al., 2007). In soil and sediments environments, metal oxides and bacteria tend to be associated with each another. Interactions between HS and bacteria (Lipczynska-Kochany 2018 and refs) as well as processes occurring on the PRBS surface, including the sorption of HS on iron oxide-bacteria composite (Jiang, et al., 2014), are still not well understood. Potential role of CC change on complicated processes, relevant for the in-situ remediation of groundwater, are yet to be explored.

6. Summary

Humic substances (HS) are the major carbon pool in the biosphere and their important role in the global warming has been recognized and extensively studied. However, much less attention has been paid so far to effects on the surface water and groundwater quality, which may result from the climate induced impact on HS. Increase in temperature and enhanced biodegradation of SOM leads to an increase in the production of DOM, while the flooding and runoff export it from soil to rivers, lakes and groundwater. Increased concentration of DOM in water will stimulate microbial growth and it may enhance biodegradation of pollutants in water. However, it may have also negative effects, including an inhibition of solar disinfection in surface waters. Increase in DOM concentrations in the source freshwater may create problems for drinking water production facilities.

Climate induced changes in the structure of HS, resulting from their microbial transformations, as well as changes in acidity and other environmental factors will alter the character of binding between HS and contaminants. As a result, re-mobilization of metals and organic pollutants, and their subsequent wash-up from the soil and sediments surfaces may be expected. There is a concern that CC will have broad negative impacts on the behavior and fate of many freshwater contaminants. Both, natural and constructive wetlands are expected to be influenced and the in-situ surface water treatment (CWs) may be upset. It is also anticipated that, as a result of the surface water shortage, demand for groundwater will increase. Groundwater quality and its effective remediation are therefore of a great importance. Processes relevant to the groundwater treatment conducted in-situ are strongly dependent on the environmental conditions. Changes in acidity and other environmental factors will alter the character of binding between HS, contaminants and minerals. Therefore, CC (and increased concentrations of DOM) may have a significant influence on processes occurring in subsurface and it may affect the performance of PRBs, which are usually placed in the ground for decades. It can be expected that, as a result of CC, the quality of source freshwater will decline, what will affect the production of drinking water and it may increase the treatment cost.

7. Conclusions

CC is expected to have a significant impact on HS and on the quality of freshwater. As a result of the CC induced biodegradation of SOM, and an enhanced concentration of dissolved HS in freshwater, microbial growth may be stimulated and biodegradation of pollutants in water can be enhanced. On the other hand, negative effects may be also expected, including an inhibition of solar disinfection in brown lakes as well as an impact on the treatment of freshwater in-situ. Complex and still not fully understood, natural attenuation processes may be affected in a way difficult to be predicted. It is possible that, depending on the local conditions, toxic pollutants may be re-mobilized from sediments and/or from some PRBs surface, increasing contamination in the groundwater systems. Many of the possible CC effects, described in this article, have yet to be explored and understood. Hopefully, the enormous potential for interesting, multidisciplinary research will encourage readers of this review to conduct studies in this important and still largely overlooked research area.

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